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Chemistry and Physics of Glass

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I. INTRODUCTION

This report summarizes work completed under the sponsorship of ARPA Order 418 during the first six months of 1972. Active areas of research include (1) the structural characterization of a variety of glasses by advanced methods of X-ray and neutron diffraction, (2) studies of the effects of high energy ion-implantation on the strength of silicate glasses and (3) an investigation of the properties of the luminescence observed during the fracture of glasses at very high stress levels.

The investigations into the structure of glasses have continued to produce significant and surprising results. Earlier work at NRL under this contract had indicated that fused silica possessed short range order up to at least 15 Å and was better described in terms of a crystallite model rather than the random network model of Zachareisen. X-ray and neutron diffraction investigations of other silicate and semiconducting glasses conducted during the current reporting period strongly suggest that the similarity between crystals and glasses is quite a general property. This experimental evidence is extremely important for understanding the relevant physical properties of glassy materials. Theoretical calculations should be based on a model which assumes a random distribution of macroscopic crystallites rather than atoms or molecules.

Work on the ion-implanted glasses has also progressed. Higher doses in SiO_2 have resulted in a factor of 2 increase in tensile strength. The profiles of the implanted species have been measured by use of chemical etching and the monitoring of color center (ESR of E' centers) intensity. Damage has been shown to be consistent with a bond ionization mechanism. No unique optical or ESR absorption has been observed which can be attributed to knock-on type damage. Annealing studies have been made,

which indicate the radiation damage can be healed without the diffusion of implanted ions.

An investigation into the luminescent properties of fracturing glasses was initiated during this period. Measurements are being made on specimens under both tensile and compressive stresses. Efforts are now centered on achieving sufficiently high stresses ($\approx 5 \times 10^5$ PSI) in the glasses to allow observation of the emitted light.

II. PROGRESS

A. Structure of Glass

Glasses have generally been depicted as random networks where only a few of the shortest interatomic distances correspond throughout the sample to those present in a crystalline phase. However, new data-reduction techniques have been developed at NRL for obtaining from the diffraction patterns of glasses heretofore unresolved structural information. This new information indicates that glasses and crystals are very similar on the atomic level.

The major improvements in the data-reduction procedures have been effected by the introduction of physical and mathematical criteria which must be satisfied by the distribution of distances. For example, distances smaller than the smallest bonded distances should not appear in the distribution, and at sufficiently large distances, all distances should occur with equal probability. These procedures have been employed in the recent investigations of silica and germania glasses. The distributions of interatomic distances obtained for these glasses were found to be consistent with a structure composed nearly entirely of ordered regions similar to the crystalline polymorph of silica, tridymite, having dimensions up to at least 20 Å and bonded together efficiently in configurations analagous

to twinned crystals. The techniques of X-ray and neutron diffraction were employed in the analysis.

Investigations of other silicate and semi-conducting glasses now in progress strongly suggest that the similarity between crystals and glasses is a quite general property. Diffraction data obtained with the glass of arsenic triselenide indicates that this glass also is composed of ordered regions of up to at least 20 Å with the same atomic arrangements as are present in the crystalline phase. The silicate glasses, $NaAlSi_3O_8$ and $KAlSi_3O_8$, now being investigated are also highly ordered systems that should provide additional insight into the nature of the structure of glasses.

B. Ion Implantation of Glasses

An increase in the tensile strength of glass by ion implantation is expected provided that the compressive layer produced by the ion stuffing process is not destroyed by relaxation processes associated with radiation damage. It is therefore important to understand the nature of the radiation effects in the glasses chosen for the glass strengthening tests.

Four different fused silica glasses (Suprasil, Infrasil, Herron UV grade and GE 125) were employed in the ion implantation study. Fluences ranged from .54 X 10^{15} to 7.7 X 10^{16} ions/cm^2 at energies of 60 keV to 3 MeV. This corresponds to peak volume densities of 10^{17} to 10^{21} implanted atoms per cubic centimeter. The average strength in those samples irradiated at the highest dose levels was observed to increase by 50%. One sample showed a 100% strength increase.

The nature of the radiation damage in the silica samples has been studied in more detail. The optical absorption bands in the implanted samples are found at 2350 Å (5.7 eV) and 2150 Å (5.9 eV).

These are the E' bands which are prominent in bulk samples. The implanted samples also show a shift of the optical absorption edge to longer wavelengths in the vacuum ultraviolet. The radiation band at 7.6 eV in bulk silica has not been resolved in the ion implanted layers. A strong ESR signal near g = 2 has been identified as the E' resonance. Annealing studies have shown that the ESR and optical signals bleach out almost entirely after one hour at 500°C. This is a sufficiently low temperature to insure the maintenance of the surface compression layer. The profile of the implanted species has been measured indirectly by monitoring the strength of the color centers per increment of surface etched with hydrofluoric acid. The ESR signal was used rather than optical absorption because of the superior detection sensitivity. Damage during the ion implantation process proceeds by ionization and knock-ons. The LSS theory predicts the strength of the electronic stopping processes relative to nuclear stopping power for a given host material and accelerated ion. Comparison of the experimental profile of radiation damage in SiO_2 with the ion energy loss predicted by the LSS theory confirm that the principal damage mechanism in SiO_2 is ionization. This is also supported by the failure to observe any new absorption bands in ion implanted SiO_2 when compared to the damage in X-irradiated material.

Strength tests were also made on 1 inch disks of Suprasil which had been irradiated with 40 kV X-rays in an effort to differentiate between the effects of radiation damage and surface compression on glass strength. The X-irradiated samples were found to differ little in strength with the control group of untreated samples.

The work on the ion implantation of Pyrex (Corning 7740) glass has been slowed by problems with the NRL Van de Graaff accelerators. It is anticipated that the Pyrex samples will be run on the 60 or 100 keV

machine starting in mid August. In the interim, work is being done to characterize the nature of the radiation damage in Pyrex samples which have been subjected to X-rays.

C. Luminescence of Glass during Fracture

Outwater and Gerry reported luminescence of Pyrex glass rods failing at what appeared to be limiting compressive stresses (450,000 - 550,000 psi)*. The light was emitted from the areas adjacent to the fracture, and was sufficient to allow an "auto" photo to be made of the fracture. No reason was given for this phenomenon. Similar observations have been reported (unpublished) at high stress levels for other materials, apparently including failure under tensile as well as compressive stresses. If this luminescence can be substantiated, study of it might give substantial insight into the fracture process; e.g., does it vary with stressing (tension versus compression), test atmosphere, composition, etc.?

To see if such emission occurs, soda lime, borosilicate and fused silica glasses are being tested in three point bending in dark room conditions with an open lens polaroid camera and/or a photomultiplier tube to record any emission of light. Rectangular bars (approximately 0.1" X 0.2" in cross section) were machined, then etched with various concentrations of hydrofluoric acid. This technique improved strengths, but typically only to 20-40 ksi., with one failure as high as 72,000 psi. No emission was detected. Examination showed that the failures generally initiated at the edges of the etched bars, apparently due to irregularities there, so round rods were used to eliminate such edge problems. Trial etching of round rods raised the average stress value but did not raise

*Outwater and Gerry, "The Effects of High Uniaxial Compressive Stress on Glass," University of Vermont, Contr. NONR3219 (01) (X)

the higher failure stresses. However, initial flame polishing of round fused SiO_2 rods has given maximum failure stresses of 212,000 psi. No indication of light emission has been observed at this level of stress. Improvement of flame polishing and possible use of a special NRL gas phase polishing technique will be investigated to achieve higher stresses, hopefully > 400,000 psi where such luminescence has been reported.

PUBLICATIONS AND PRESENTATIONS

1. Tridymite-like Structure in Silica Glass. J.H. Konnert and J. Karle, Nature Physicel Science, 236 , 92 (1972).

2. Crystalline Ordering in Silica and Germania Glasses. J.H. Konnert, J. Karle and G.A. Ferguson (submitted to Science).

3. The Effect of Ion Implantation on the Tensile Strength of Silica Glass, G.H. Sigel, Jr. Bull. Am. Phys. Soc., Ser.II 17, 287 (1972).